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Lattice effects in $HoVo_3$ single crystal

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Abstract

We report the study of lattice effects in the Mott insulator $HoVO_3$ performed by means of linear thermal expansion on a single crystal in the temperature range 10–290 K. The holmium orthovanadate $HoVO_3$ reveals gradual orbital ordering (OO) below $T_{OO} = 200$ K and orders antiferromagnetically at $T_N = 113$ K. A first-order structural phase transition takes place at $T_S \sim 38$ K, which is probably accompanied by change of the OO type and hence the type of antiferromagnetic spin ordering.

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Keywords: Thermal expansion; Mott localisation; Phase transitions—structural

The transition-metal oxides with the perovskite structure ABO_3 have been intensively studied during the last years because of their intriguing properties, as colossal magnetoresistance, high-temperature superconductivity, etc. Among them, vanadium oxides display a very rich phenomenology related to the spin, orbital and lattice degrees of freedom. $HoVO_3$ belong to the family of V^{3+} oxides derived from YVO_3. Since the Ho^{3+} and Y^{3+} ions have very similar ionic radius, the structural and electronic properties of both compounds are supposed to be similar. Indeed $HoVO_3$ reveals, similarly to YVO_3, a distorted perovskite structure (space group Pbnm) at room temperature and exhibits similar sequence of magnetic and structural phase transitions as observed in YVO_3 [1]. Yttrium orthovanadate YVO_3 presents a distorted perovskite structure. It is a Mott insulator where the 3d V^{3+} magnetic moments order antiferromagnetically (AF) below $T_N = 116$ K. At temperatures higher than $T_S = 77$ K the spin order (SO) is C-type AF (ferromagnetic coupling along *c*-axis and AF within the *ab*-planes) whereas below T_S a change to a G-type AF structure (antiferromagnetic coupling in all directions) takes place through a first-order structural phase transition accompanied by a change in the unit cell volume [2]. A Jahn–Teller-ordered state at low temperature evidences the existence of orbital ordering (OO) which symmetry changes at T_S from G-type (all d_{xy} orbitals occupied and alternatively occupied d_{yz} and d_{zx} ones) to C-type (alternative occupation within *ab*-planes and the same along *c*-axis) while cooling. In spite of the lack of SO above T_N the OO remains up to $T_{OO} = 196$ K, where a next structural phase transition takes place [3,4]. The changes of the OO structure of the YVO_3 have been proposed as the origin of the observed multiple temperature-induced magnetisation reversal processes [5].

Similar OO transitions as well as the magnetic transitions are the common feature of whole family of the RVO_3 orthovanadates (R being a rare-earth ion), whereas the first-order structural phase transition has been observed only in the compounds where R = Lu, Yb, Er, Dy [6]. In the latter work the phase transitions temperatures were reported for all the rare-earth orthovanadates except the $HoVO_3$ one.

In order to complete the phase transition diagram and have a deeper insight into the lattice and volume changes associated with the mentioned structural, magnetic and OO

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transitions we have performed linear thermal expansion (LTE) measurements on a single-crystalline $HoVO_3$ synthesised using floating zone method [1]. The relative length change due to thermal expansion has been measured using the strain gauge technique: the relative resistance change of a gauge fixed on the sample (in this case parallel to each of the three crystallographic axes), is proportional to the relative length change $\Delta L/L$ [7]. The measurements have been performed from 290 K down to 10 K.

The LTE along the three crystallographic axes, measured when the temperature is increased, is shown in Fig. 1(a), while Fig. 1(b) presents the temperature dependence of the LTE coefficient α, which is defined as the first derivative of the LTE. The calculated volume thermal expansion and volume expansion coefficient are displayed in Fig. 1(c). The measurements show that the LTE has strong anisotropic character. Nevertheless, the measurements along the three crystallographic directions display some common features. When increasing the temperature an abrupt anomaly is observed at $T_S = 38$ K, which corresponds to a simultaneous contraction along the *a*- and *c*-axes ($\Delta L/L \approx 0.20\%$ and 0.23%, respectively), together with an expansion along the *b* direction ($\Delta L/L \approx 0.57\%$). The contractions and elongations observed in $HoVO_3$ are almost 20% larger than the respective values measured in YVO_3 [7], whereas the transition temperature is significantly lower. The comparison of the LTE measurements, performed while heating and cooling, reveals the existence of hysteresis in the structural transition, and therefore confirms the first-order character of this transition. On increasing the temperature, the progressive expansion of the *a* and *c* lattice parameters and the simultaneous decrease of the *b*-axis take place. Very weak anomalies (slope decrease) are detected in the LTE at the magnetic order transition temperature $T_N \approx 113$ K. Nevertheless the magnetic order transition is nicely revealed in the $\alpha(T)$ dependencies, shown in Fig. 1(c), as a decrease of absolute value of volume thermal expansion coefficient by $\alpha \sim 0.5 \times 10^{-5}\,K^{-1}$. Moreover, a drastic slope change is observed at $T_{OO} = 200$ K, which coincides with the appearance of a sharp peak in the specific heat measurements, which was associated with the OO transition [1]. This anomaly is specially marked in the LTE measured along the *b*- and *c*-axes. Nevertheless the $\alpha(T)$ dependencies show that all three crystal directions are involved in creation of the G-type OO.

The corresponding relative volume change with respect to the initial sample volume, Fig. 1(c), is $\Delta V/V \approx 0.15\%$. The thermal dependence of the volume shows a drastic change at T_S already seen in the LTE. In contrary to the linear expansion the increase of the $HoVO_3$ crystal volume at T_S is smaller than that measured in YVO_3 by 25%. Similar to YVO_3, $HoVO_3$ also reveals absence of significant volume change at the highest temperatures, which unambiguously indicate that the transition taking place at T_{OO} is really an effect related to the ordering of the electronic orbitals.

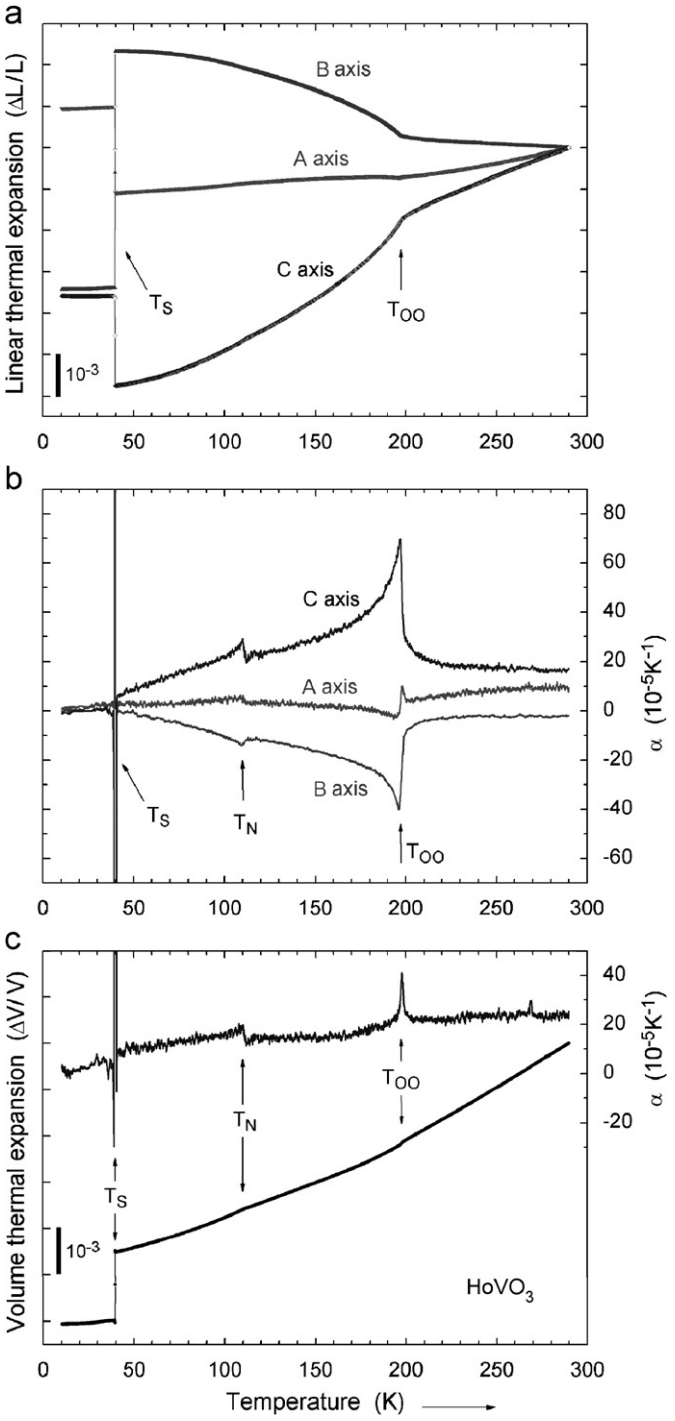

Fig. 1. (a) Linear thermal expansion, (b) linear thermal expansion coefficient, α, and (c) volume thermal expansion and its coefficient (upper curve) of a $HoVO_3$ single crystal. The temperatures of the OO (T_{OO}), magnetic order (T_N), and the first-order structural (T_S) transitions are marked by arrows. All presented results have been taken while heating. The absolute values of α as well as volume expansion coefficient are going to infinity at T_S (their values are much higher than the graph limits).

In summary, we measured LTE of a $HoVO_3$ single crystal in the temperature range 10–290 K. LTE measurements showed an anisotropic character and gave direct evidence of the creation of the OO state below

$T_{OO} = 200\,K$ and of the abrupt change of structure at $T_S = 38\,K$. The magnetic (spin) ordering was also recognised in the temperature dependence of the LTE coefficient α. The reduction of $T_S = 38\,K$ for R = Ho compared with 77 K for R = Y is remarkable. The Shannon radius of Ho^{3+} is very similar to the radius of Y^{3+}. Therefore, the difference in spin/orbital reorientation temperatures, T_S, cannot be ascribed to an ionic size effect of the rare earth ion. On the other hand, both neighboring 4f elements Dy and Er, exhibit a $T_S \sim 67\,K$, which is similar to the value for R = Y. Therefore, the magnetic moment or other differences between yttrium and the rare earth elements can also not easily explain the difference in T_S. Finally, T_S is much larger than the magnetic ordering temperature of the 4f sublattice, which is below 10 K for R = Ho. An explanation of the trends of T_S but also of T_{OO} through the rare earth series, requires further analysis.

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